

Computer Simulations of Carbon Nanostructures under Pressure

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Several interesting phenomena are observed when materials are put under pressure. The goal is to achieve modification and control over their mechanical and electronic (conduction) properties. Within this spirit, we have recently focused our attention into how carbon nanostructures respond to hydrostatic pressure. We performed Monte Carlo simulations with the Tersoff potential of various free-standing carbon nanostructures. These range from fullerenes, onions and carbon spheres to nanotubes and nanodiamonds. Our simulations show that the nanostructures undergo some notable structural modifications.

INTRODUCTION

In recent years, novel carbon materials are studied intensively because of their enormous potential utility. They display unique structural, mechanical and electronic properties. Much research has been done since the mid 80's when C_{60} was discovered [1]. New perspectives conjured after finding the 4th form of Carbon: nanotubes [2]. These structures have inspired interesting advances in science and guided the visualization and production of similar other stable structures such as peapods (C_{60} inside CNT) [3] and a variety of fullerenes. In these categories of Carbon forms, Carbon onions[4] and Carbon spheres[5] are also included.

Carbon nanotubes (CNT) display a unique structure and exhibit exceptional properties such as high stiffness and flexibility, tunable electrical conduction between metallic and semiconducting states. Fullerenes, on the other hand, are ideal for manipulating materials on a molecular scale in order to form or tailor structures of this size. Regarding the hybrid forms of CNT and fullerenes, namely peapods, their tunable electronic properties must be underlined, since they exhibit electronic features additional to that of CNT, which are strongly dependent on the location of fullerenes along the tube. In addition, Carbon onions can be used in energy storage and fuel cells and as immensely tiny ball bearings that may be used in nanomachines built on the scale of molecules. Carbon spheres [5], which consist of an amorphous Carbon (a-C) core and graphine (fullerene-like) shells, might find potential application such as catalyst carriers, lubricants and hydrogen storage materials.

On the other hand, a hybrid sp^2 - sp^3 Carbon nanocluster are bucky diamonds. These are Carbon nanoparticles with a diamond core of a few nm and a fullerenelike surface [6]. Bucky diamonds are expected to be present at meteorites in residues of detonation as well as inclusions of diamondlike films. Quantum confinement effects are present if these bucky diamonds become smaller than 2 nm. An open, though, question is their behaviour if they are coalesced, suspended or interconnected.

All of the above nanostructures are potential building blocks of nanotechnology. Many of them have been extensively investigated theoretically and experimentally to discover their properties. Application of pressure has been used in the case of nanotubes [8] particularly if they form bundles [9]. The pressure, though in most cases is axial, contrary to our calculations.

In the current study, we aim to examine how Carbon nanostructures respond under pressure and reveal a transformation path. Hydrostatic pressure is, thus applied and the structural deformation are examined. Estimations on critical values of pressure at which these deformations occur will also be presented. An intimation, finally, of the coalescence of bucky diamonds under pressure will be made as it is essential to know the way that nanoscale units join. These issues are interesting as they can lead to different configurations and provide ways of modification and control of the electronic properties of the Carbon nanostructures [10].

METHODOLOGY

Computer simulations using empirical potentials are effective methods for the analysis of structural and mechanical properties of complex systems. The Monte-Carlo (MC) technique, more specifically, is able to handle large systems and is preferable for statistical accuracy. A canonical (N,P,T) ensemble was used in order to apply pressure to the system. In this approach, the atomic interactions were modeled through the Tersoff potential [7].

In addition to the Tersoff potential the Lennard-Jones potential was also implemented into the calculations to

simulate the long range Van der Waals forces wherever they exist (i.e. among C_{60} molecules and nanotubes or a-C atoms and nanotube atoms, and more generally between sp^2 cages). The parameters of this potential were given by Lu and Wang [13] : $\epsilon=2.964$ meV, $\sigma=3.407$ Å, and have been used successfully to describe the bulk properties of solid C_{60} and multiwall nanotubes [13, 14])

RESULTS - DISCUSSION

Hydrostatic pressures ranging from 0 to 100 GPa were applied on Carbon nanostructures. As a first step we use only one nanostructure per simulation. The simulation temperature is 300 K, while calculations for 1500K and 2000K in the case of nanodiamond coalescence were also carried out.

The effect of pressure on single wall nanotubes (swnt) has already been studied, although in most cases the pressure was axial [8, 11]. The resulting structures consist of a series of segments resembling deformed ellipsoids, connected with narrowed junctions and are actually buckled. This buckling is noticeable for pressures higher than 3 GPa and range up to 5-7 GPa. Some sp^3 sites the approaching shells are also formed. These sp^3 atoms are mostly clustered and are located on the narrowed junctions. An elastic recovery of these buckled swnts upon decompression was found, although as the pressure increases some defects still exist.

Multi-wall nanotubes (mwnts) under pressure show similar trends, where sp^3 hybridization is again visible. These results coincide with another study published while we were analyzing our results[12]. The buckling of mwnts is visible at relative high pressures. The critical pressure is about one order of magnitude higher than in the case of swnts. It is calculated around 30-50 GPa. Long range van der Waals (vdW) forces are present between the adjacent walls of a mwnt. These may play a role in the significant increase of the buckling pressure.

An analogous increase of the buckling pressure was evident also in the case of compressed peapods. Another point here, is that as pressure continues to rise the surrounding swnt may bond to the inner array of C_{60} s. Focusing at this inner array shows a coalescence of the fullerene molecules while buckling takes place. An example of a compressed (12,12) peapod at a pressure of 70 GPa, is shown in Fig.1a. The inner coalesced C_{60} s at this pressure is shown in Fig.1b.

Fullerenes, on the other hand, spherical and oval shaped were also put under pressure. The former obtain a shape similar to a buckled star, while the latter a more rectangular one. An initially spherical (C_{540}) and an oval shaped (C_{100}) fullerene with diameters of about 21 and 11.6 Å, correspondingly are shown in Fig.2. Their transformation takes place at modest pressures \approx 5-6 GPa.

The effect of hydrostatic pressure on Carbon onions is similar to that of fullerenes and propagates through the shells leaving almost unaffected the inner shell which in our simulations corresponds to small fullerenes of approximately 0.8-1nm size, like C_{60} or C_{70} . Carbon onions compressed at around 50 GPa develop a surface similar to that of spherical onions.

One remark concerning the configuration of Carbon spheres is that the internal amorphous Carbon (a-C) forms a shell resembling that of the fullerene, having a high percentage of 6-fold rings. No bonding takes place among the inner and the outer shell. As the pressure increases up to approximately 80-100 GPa the spheres, both the fullerene shell and the a-C core, flatten at their edges and turn into cubes (Fig.2).

A final preliminary result that will be given here is the coalescence of diamond nanocrystals. The open question is whether they develop a reconstructed surface (and become bucky diamonds) even if they are compressed. In order to give an answer, we firstly compressed under various pressures a free standing spherical nanodiamond of a 6.8 Åradius. As we raised the temperature up to 1500K the fullerenelike reconstruction occurred even under the effect pressures up to 50-70 GPa. The same procedure was carried out for two diamond nanocrystals at various small distances of 3-10 Å. The reconstruction again occurred at similar to the above, conditions. An example is given in Fig.4, where two nanodiamonds of a 6.8 Åradius are compressed and their coalescence is promoted. In the case, finally of relative small temperatures close to 300-500K, the bonding among the two nanostructures is visible, but no reconstruction occurs.

CONCLUSIONS

Results regarding the effect of hydrostatic pressure on different free-standing Carbon structures of the nanometer scale were presented. Their structural transformations were studied, which may reveal a path to the modification of their electronic properties. A modest buckling pressure for single wall nanotubes were found, which increased significantly for structures including van der Waals forces. Finally, a preliminary study on the coalescence of nanodiamonds showed that they develop a fullerenelike reconstructed surface even under pressure.

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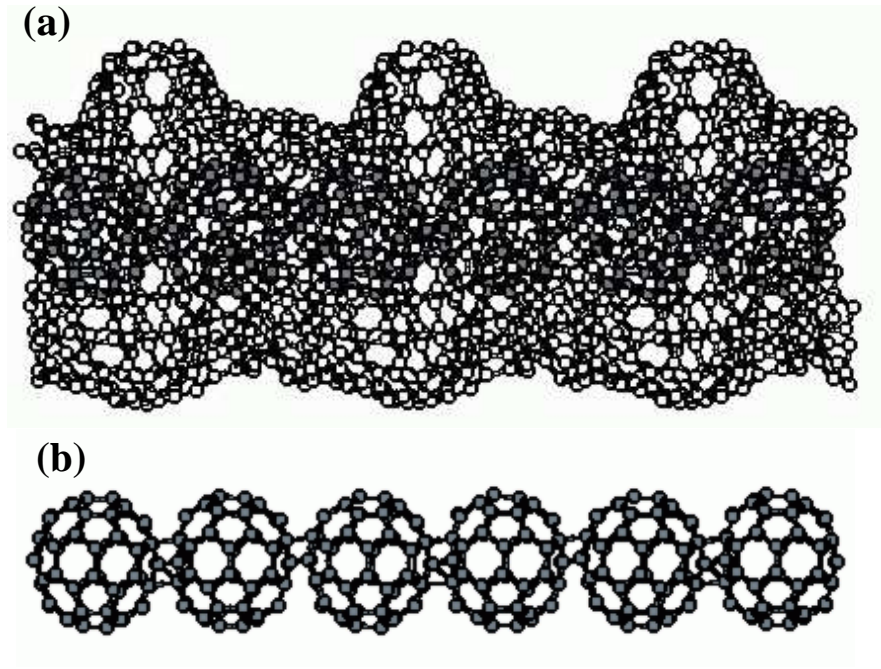


FIG. 1: Peapod under a pressure of 100GPa (a). The coalesced array of the internal C_{60} s is shown in (b).

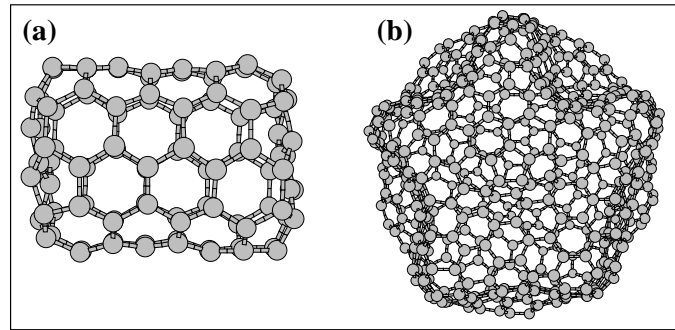


FIG. 2: Figures of C_{100} and C_{540} after their compression at ≈ 5 GPa. Their initial shape was oval and spherical, correspondingly.

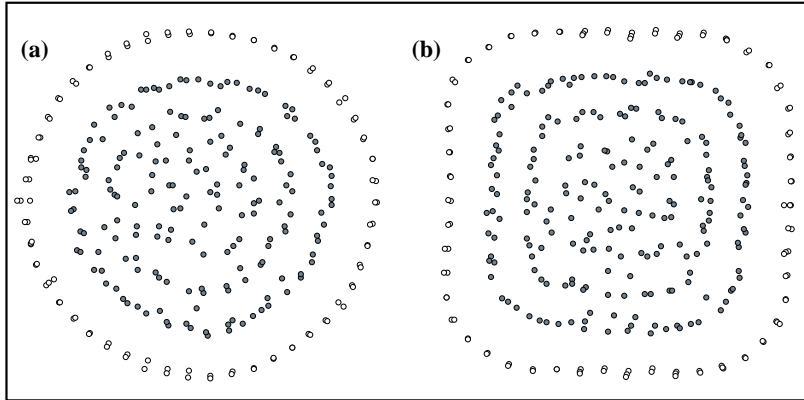


FIG. 3: Views of Carbon spheres (a) before and (b) after the exertion of 100 GPa. The internal grey atoms correspond to the a-C core.

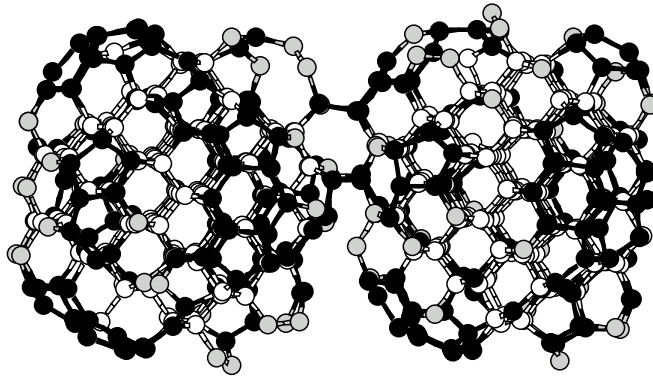


FIG. 4: Coalescing of 2 nanodiamonds (each with a radius of 6.8 Å) at 1500K under a pressure of 20 GPa. White atoms correspond to sp^3 bonding, while the black ones to sp^2 . Bonds close to 1.4-1.5 Å are formed.